addition to elucidating the mechanism of COHED, our results provide strong support for the existence of an enol intermediate in metal-dependent $\beta$-decarboxylase reactions.

**Acknowledgment**. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society (23993-AC4), and the National Institutes of Health (Grant GM41239) for their support of this research. In addition, we thank Steve D. Sorey (Department of Chemistry, The University of Texas) for his expert assistance in the acquisition of the $^1$H NMR spectra.

---

# Stereochemistry of a Cyclohexyllithium Reagent. A Case of Higher Configurational Stability in Strongly Coordinating Media[1]

Hans J. Reich,* Marco A. Medina, and Michael D. Bowe

*Department of Chemistry*
*University of Wisconsin*
*Madison, Wisconsin 53706*

*Received September 8, 1992*

The use of configurationally defined organolithium reagents in ether solvents has only been possible for the exceptional cases of vinyl,[2] cyclopropyl,[3] $\alpha$-alkoxyalkyl,[4] and more recently $\alpha$-selenoalkyl,[1a,5a] and $\alpha$-aminoalkyl[6] lithium reagents.[7-9] Although early studies by Letsinger[10] and Curtin[11] showed that even secondary alkyllithium reagents lacking such structural features can be prepared in optically active form if conditions are mild and a hydrocarbon solvent is used, they made the discouraging observation that the *rate of racemization was greatly accelerated by small amounts of ether.* Higher configurational lability of normally isomerically stable vinyllithium[2b,c,11] and cyclopropyllithium reagents[12] in the presence of polar solvents has also been reported.

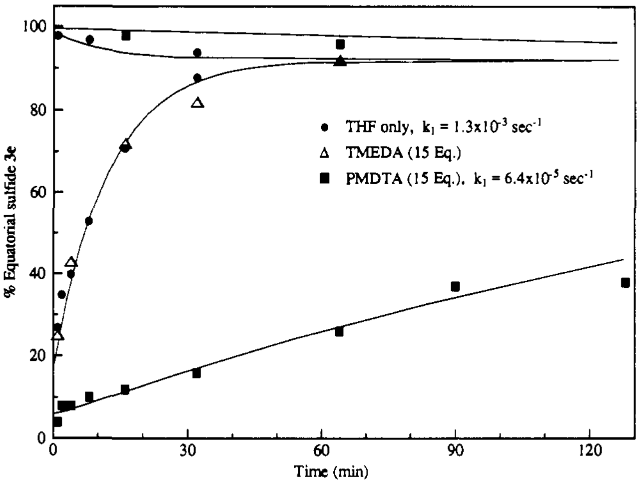
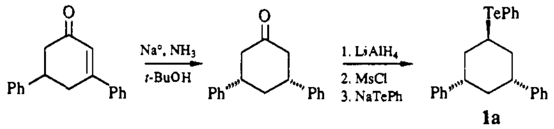


**Figure 1**. Formation, equilibration, and trapping of axial and equatorial lithium reagents **2a** and **2e** formed from **1a** and **1e**. The points are the ratios of isolated methyl sulfides **3a** and **3e**. The lines are best fit pseudo-first-order calculated ratios, using the rate constants shown ([**1**] = 36 mM).

We report here that axial and equatorial cyclohexyllithium reagents[8a] can be formed with high isomeric purity *in THF* and maintain configurational integrity long enough for laboratory time scale trapping experiments. We chose the lithium/tellurium exchange reaction[13] for this study, since it is among the fastest of all Li/M exchanges (only slightly slower than the Li/I[1b,d]), and tellurides have advantages over iodides in ease of preparation and lower reactivity in $\alpha$- and $\beta$-elimination.



**1a**

The axial and equatorial isomers of 1-(phenyltelluro)-*cis*-3,5-diphenylcyclohexane (**1**) were easily prepared from the corresponding alcohols by mesylation and $S_N2$ substitution with sodium phenyltellurolate.[14] Treatment of **1a** with at least 3 equiv of *sec*-butyllithium resulted in fast (<30 s) cleavage of both C–Te bonds at −78 °C to give solutions of predominantly the axial lithium reagent **2a**, as indicated by trapping with dimethyl disulfide to form **3a** and **3e** in combined yields of 80% or better. Di-*sec*-butyl telluride and phenyllithium were also formed, and some unreacted *sec*-butyllithium remained. Apparently inductive withdrawal by the phenyl substituents provides some stabilization of **2** relative to *sec*-butyllithium. However, if less than 3 equiv of *sec*-butyllithium was used, significant amounts of 1-*sec*-butyltelluro-3,5-diphenylcyclohexane remained in the reaction mixture.

The solution of **2a** formed in this way isomerized to **2e** with a half-life of ≈9 min at −78 °C, reaching the equilibrium mixture of 8/92 **2a**/**2e** in 1 h.[8a] The equatorial telluride **1e** similarly gave

---

[1] (a) Reich, H. J.; Bowe, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 8994. (b) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414. (c) Green, D. P. PhD Thesis, University of Wisconsin, Madison, 1989. (d) Reich, H. J.; Green, D. P.; Phillips, N. H.; Borst, J. P. *Phosphorus Sulfur* **1992**, *67*, 63.

[2] (a) Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883. (b) Panek, E. J.; Neff, B. L.; Chu, H.; Panek, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 3996. (c) Knorr, R.; Lattke, E. *Tetrahedron Lett.* **1977**, 3969. (d) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785.

[3] (a) Applequist, D. E.; Peterson, A. H. *J. Chem. Soc.* **1961**, *83*, 862. (b) Applequist, D. E.; O'Brien, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 743. (c) Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3283. (d) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1984**, *25*, 2415. (e) Tanaka, K.; Minami, K.; Funaki, I.; Suzuki, H. *Tetrahedron Lett.* **1990**, *31*, 2727.

[4] (a) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. (b) Sawyer, J. S.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 3376. (c) Hoppe, D.; Hintze, F.; Tebben, P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1422. (d) Rychnovsky, S. D.; Mickus, D. E. *Tetrahedron Lett.* **1989**, *30*, 3011.

[5] (a) Hoffmann, R. W.; Julius, M.; Oltmann, K. *Tetrahedron Lett.* **1990**, *31*, 7419. (b) Hoffmann, R. W.; Ruhland, T.; Bewersdorf, M. *J. Chem. Soc., Chem. Commun.* **1991**, 195.

[6] (a) Pearson, W. H.; Lindbeck, A. C. *J. Am. Chem. Soc.* **1991**, *113*, 8546. (b) Kerrick, S. T.; Beak, P. *J. Am. Chem. Soc.* **1991**, *113*, 9708. (c) Chong, J. M.; Park, S. B. *J. Org. Chem.* **1992**, *57*, 2220.

[7] Primary organolithium reagents invert configuration on the NMR time scale. (a) Witanovski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 737. (b) Fraenkel, G.; Beckenbaugh, W. E.; Yang, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 6878.

[8] Secondary (including cyclohexyl) alkyllithium reagents in ether and pentane are stable on the NMR timescale. (a) Glaze, W. H.; Selman, C. M. *J. Org. Chem.* **1968**, *33*, 1984. (b) Fraenkel, G.; Henrichs, M.; Hewitt, M.; Su, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 255.

[9] For previous efforts to prepare stereochemically defined cyclohexyllithium reagents, see:[8a] (a) Lambert, J. B.; Majchrzak, M. W.; Rosen, B. I.; Steele, K. P.; Oliver, S. A., Urdaneta-Pérez, M. *Isr. J. Chem.* **1980**, *20*, 177. (b) 2-Norbornyllithium appears to have some configurational stability in pentane: Applequist, D. E.; Chmurny, G. N. *J. Am. Chem. Soc.* **1967**, *89*, 875. Bornyl and isobornyl chloride give identical lithium reagent mixtures: Maercker, A.; Schuhmacher, R.; Buchmeier, W.; Lutz, H. D. *Chem. Ber.* **1991**, *124*, 2489. (c) Cyclohexylmagnesium compounds: Goering, H. L.; McCarron, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2287.

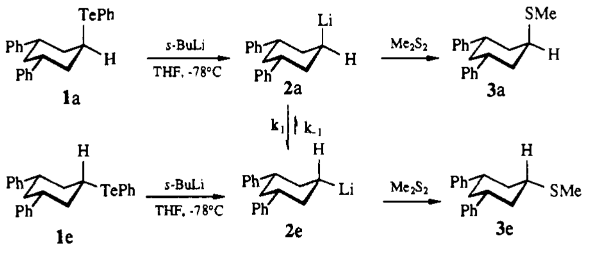
[10] Letsinger, R. L. *J. Am. Chem. Soc.* **1950**, *72*, 4842.

[11] Curtin, D. Y.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 1967.

[12] (a) Koebrich, G.; Merkel, D.; Imkampe, K. *Chem. Ber.* **1973**, *106*, 2017. (b) Hoell, D.; Schnieders, C.; Muellen, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 243.

[13] Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314. Tomoki, H.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187.

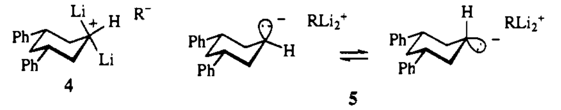
[14] The 3,5-diphenylcyclohexyl system is well suited for these studies, since, in contrast to the 4-*tert*-butylcyclohexyl system, 99% or better isomerically pure materials can routinely be obtained by crystallization, and structure determination by NMR is easy and reliable.[1a]



a preponderance of equatorial lithium reagent **2e** and equilibrated to the same 8/92 mixture of **2a** and **2e** (see Figure 1). These results represent the first example of a non-cyclopropyl hydrocarbon alkyllithium reagent with useful configurational stability on the laboratory time scale in THF or any ether solvent.

The rate of equilibration was accelerated by lithium iodide and was strongly dependent on the total organolithium concentration.[12b] Reasonable pseudo-first-order kinetics were obtained when the concentration of *sec*-butyllithium was optimum (36 mM, $t_{1/2}$ = 9 min), as shown in Figure 1. At 96 mM, $t_{1/2}$ was 3 min, at 24 mM, approximately 18 min, but considerable scatter was observed at both the higher and lower concentrations, the former because the rate was too fast, and the latter because the concentration of RLi was too low for accurate work.

A reasonable interpretation of this concentration dependence is that the inversion process involves an aggregation state higher than that present in THF. If **2**, like *sec*-butyllithium,[15] is largely monomeric in THF, then the inversion may involve a dimer (this fits our rate data best) or a higher aggregate. The concentration dependence of primary Grignard reagent inversion has been rationalized by invoking aggregate formation.[16] An aggregate may provide mechanistic opportunities for moving a cation from one face of a carbanion to the other not available to a monomer, for example, by formation of a rapidly inverting free carbanion **5** or a triple ion intermediate such as **4** with a symmetrically dilithiated planar carbanion,[17] or by related pathways as explored theoretically for methyllithium dimer.[18]



We have tested the aggregation hypothesis. A complexing agent that effectively prevents dimerization might enhance the configurational stability of **2a** by preventing aggregate-based lithium exchange. The tridentate ligand *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA) is uniquely suited for the purpose: it is a strong complexing agent[1c,19] and is capable of occupying the three free coordination sites of a monomeric organolithium reagent, thus inhibiting dimerization.[15,20]

The cleavage of the tellurides **1a** and **1e** was repeated in the presence of PMDTA (1/3/15 ratio of telluride, *sec*-butyllithium, and PMDTA), with the results shown in Figure 1. The isomerization rate was reduced by a factor of 20, with a half-life for equilibration longer than 2 h. The equilibration constant was not significantly affected by the presence of PMDTA (a ratio of 7/93 **3a**/**3e** was obtained at −45 °C). Furthermore, the rate of isomerization was unaffected by an 8-fold increase in the concentration of *sec*-butyllithium, provided that at least a 5-fold excess of PMDTA over lithium was maintained.[21] Under optimum conditions at −78 °C with short reaction times, **1a** gave 94% axial sulfide **3a**, and **1e** gave 98% equatorial sulfide **3e**. In contrast, the rate of epimerization increased when run in ether/THF mixtures compared to pure THF (most lithium reagents form higher aggregates in ether than in THF). The bidentate complexing agent tetramethylethylenediamine (TMEDA, 5 equiv per RLi) produced no significant change in the rate of isomerization of **2a**.[22]

We believe that this is the first example in which configurational isomerization of a lithium reagent was slowed by increase in the strength of lithium coordination.[23] However, the configurational isomerization of neohexylmagnesium chloride[16a] and 3-cyclohexenylmagnesium bromide is slower in diglyme and THF than in ether.[16a] We speculate that there may be two "islands" of relatively high configurational stability for alkyllithium reagents as solvent polarity is changed. One is in hydrocarbon solvents in which the charge separation needed for C–Li bond reorganization is energetically costly, and a second is in more polar solvents containing predominantly monomeric species where aggregate-assisted isomerization is inhibited, as proposed in the current study. One might anticipate that further increases in solvent polarity could again facilitate isomerization by stabilizing separated ion pairs, the mechanism usually invoked for polar-solvent-accelerated isomerizations.[2b,c,6a,c,12]

**Acknowledgment.** We thank the National Science Foundation for support of this work.

---

[15] Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.

[16] DNMR studies of alkyl Grignard reagents:[7a] (a) Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4878. (b) Pechhold, E.; Adams, D. G.; Fraenkel, G. *J. Org. Chem.* **1971**, *36*, 1368. (c) Maercker, A.; Geuss, R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 270.

[17] Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827. Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987**, *109*, 6524. Collum, D. B.; Romesberg, F. E. *J. Am. Chem. Soc.* **1992**, *114*, 2112. Collum, D. B.; Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 5751.

[18] Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1978**, 137.

[19] Lappert, M. F.; Engelhart, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1323. Klumpp, G. W.; Luitjes, H.; Schakel, M.; de Kantner, F. J. J.; Schmitz, R. F.; Hommes, N. J. R. v. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 633.

[20] (a) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 6190. (b) Johnels, D.; Edlund, U. *J. Organomet. Chem.* **1990**, C35. (c) Schümann, U.; Kopf, J.; Weiss, E. *Angew. Chem.* **1985**, *97*, 222.

[21] Use of much less than 5 equiv of PMDTA per lithium results in only partial reduction of the isomerization rate; above 5 equiv, no significant additional decrease in rate was observed.

[22] Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448. Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, Q.-Y.; Willard, P. G. *J. Am. Chem. Soc.* **1992**, *114*, 5100.

[23] The opposite is usually observed: 1-substituted cyclopropyllithium,[12] 1-styryllithium,[2b,c] (α-aminoalkyl)lithium.[6a,c]

---

## Reduction and Electrochemistry of C$_{60}$ in Liquid Ammonia

Feimeng Zhou, Christophe Jehoulet, and Allen J. Bard*

*Department of Chemistry and Biochemistry*
*The University of Texas at Austin*
*Austin, Texas 78712*

*Received March 23, 1992*
*Revised Manuscript Received November 16, 1992*

We report here the reduction of C$_{60}$ slurries by solvated electrons ($e_s^-$) generated electrochemically in liquid ammonia and the cyclic voltammetry (CV) of the C$_{60}^-$ solution produced. Waves corresponding to both soluble and insoluble forms of $\mathrm{C}_{60}^{n-}$ were observed, with *n* spanning the range 0–6 (depending on the supporting electrolyte used). C$_{60}$ in solvents in which C$_{60}$ and its reduced products are soluble, e.g., CH$_2$Cl$_2$, benzene, and toluene, showed up to five CV waves,[1-4] and by use of mixed solvents at low temperature, the presence of six CV redox waves for 1e$^-$

---

[1] Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

[2] Cox, D. M.; Behal, S.; Disko, M.; Gorun, S. M.; Greaney, M.; Hsu, C. S.; Kollin, E. B.; Millar, J.; Robbins, J.; Robbins, W.; Sherwood, R. D.; Tindall, P. *J. Am. Chem. Soc.* **1991**, *113*, 2940.

[3] Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

[4] Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

0002-7863/92/1514-11004$03.00/0